

O.Z. 6325

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**Process for the production of three-dimensional objects by means of laser technology and application of an absorber via inkjet processes**

The invention relates to a process for the production of three-dimensional objects from a pulverulent substrate via bonding, e.g. via fusion or sintering of portions of the substrate, where  
5 the pulverulent substrate is applied layer-by-layer, and the electromagnetic energy needed for the melting of the substrate is generated via a laser of wavelength from 100 to 3000 nm, and is passed into an absorber, by way of which it is dissipated to the subregions of the substrate. These subregions are thereby melted layer-by-layer and bond, after cooling, to give the desired  
10 molding.

A task often encountered in very recent times is the rapid production of prototypes. One method described in the prior art is stereolithography, which has the disadvantage of needing complicated support structures during the preparation of the prototype from a liquid (resin), and  
15 the disadvantage that the resultant prototypes have relatively poor mechanical properties, these being attributable to the limited number of starting materials.

The other process often mentioned in the prior art and having good suitability for rapid prototyping is selective laser sintering (SLS), which has now become widespread. In this  
20 process, polymer powders or plastics-encapsulated particles of metal, of ceramic, or of sand are selectively and briefly irradiated with a laser beam in a chamber, thus melting the powder particles impacted by the laser beam. The molten particles coalesce and solidify relatively rapidly again to give a solid mass. This process can produce complex three-dimensional bodies simply and rapidly, via repeated irradiation of a succession of newly applied layers.

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The process of laser-sintering (rapid prototyping) to realize moldings composed of pulverulent polymers is described in detail in the patent specifications US 6,136,948 and WO 96/06881 (both DTM Corporation). The SLS processes described in the prior art have the disadvantage that expensive laser technology is needed for the process. The laser functioning as energy  
30 source is extremely expensive and sensitive, as also is the optical equipment needed for the provision and control of the laser beam, for example lenses, expanders, and deflector mirrors.

A disadvantage of the known process is that it cannot use some of the lasers available on the market. In order to permit sintering of polymer powder or of particles encapsulated with plastic, a CO<sub>2</sub> laser is required, which is expensive to purchase and expensive to service, operate, and maintain. A characteristic feature of the CO<sub>2</sub> laser is the wavelength of 10 600 nm. This  
5 corresponds to the far infrared region. A complicated mirror system therefore has to be used in order to conduct the laser beam across the construction plane; in addition, the laser requires constant cooling. Optical conductors cannot be used. Specifically trained operating staff generally have to be made available. Many end users are therefore unable to use these systems. However, use cannot be made of lower-cost lasers of wavelength in the middle or near infrared  
10 region, in the visible light region, or the ultraviolet region, because these cannot generally melt plastics, or not to the extent required for laser sintering.

It was therefore an object of the present invention to develop a process which permits the lower-cost production of laser-sintered prototypes.

15 Surprisingly, it has now been found, as described in the claims, that moldings can be produced via a process using lasers of wavelength from 100 to 3000 nm if a specific absorber is selectively applied via an inkjet process to those regions to be melted of the respective layer, and passes the heat produced via the introduction of electromagnetic energy to the particles to  
20 be sintered. The laser beam may be focused as usual. However, in order to accelerate the construction process it is advantageous to use a laser which has not been particularly focused, for example a diode laser, and to achieve the selectivity solely via the application of the absorber. The precision thereby achievable, and also the speed of the process, are equal to or higher than those obtained during conventional laser sintering using the CO<sub>2</sub> laser. The process  
25 is markedly less expensive and simpler and more flexible in operation. It is also possible to use the inkjet process to give the final product other properties or to print it during the production process, for example with conductive regions or inks.

The lasers used generate electromagnetic radiation with a wavelength of from 100 to 3000 nm,  
30 preferably from 800 to 1070 nm, or from 1900 to 2100 nm, and very particularly preferably from 800 to 1000 nm (diode laser) or 1064 nm (Nd:YAG laser). The beam may be either pulsed or continuous (continuous wave). Without restricting the invention thereto, particular

mention may be made of argon lasers of wavelength 488 and 514 nm, helium neon lasers of wavelength 543, 633, or 1150 nm, nitrogen lasers of wavelength 337 nm, hydrogen lasers of wavelength from 2600 to 3000 nm, krypton lasers of wavelength from 330 to 360 nm, or from 420 to 800 nm, ruby lasers of wavelength 694 nm, KTP lasers (double-frequency Nd:YAG lasers) of wavelength 532 nm, a triple-frequency Nd:YAG laser of wavelength 355 nm, or a quadruple-frequency Nd:YAG laser of wavelength 266 nm, an alexandrite laser of wavelength 755 nm, and also YAG lasers. The YAG lasers have an yttrium aluminum garnet crystal rod as laser medium. The rod has a doping of rare earth metal, such as neodymium (Nd:YAG of wavelength 1060 nm), erbium (Er:YAG, wavelength 2940 nm), holmium (Ho:YAG, wavelength 2070 nm), or else thulium (Tm, wavelength 2074 nm), or chromium (Cr), or combinations thereof. Other examples are Tm:YLF lasers or Ho:YLF lasers, which use a different laser medium and likewise have a wavelength of about 2000 nm. It is also possible to use high-power diode lasers of wavelength from 800 to 1000 nm, or else excimer lasers of wavelength 193 nm or 352 nm. Particular excimer lasers which may be mentioned are F2 excimer lasers of wavelength 157 nm, ArF excimer lasers of wavelength 193 nm, KrCl excimer lasers of wavelength 222 nm, KrF excimer lasers of wavelength 248 nm, XeCl excimer lasers of wavelength 308 nm, and XeF excimer lasers of wavelength 351 nm.

The lasers may be solid-state lasers (examples being the ruby laser and the Nd:YAG laser), semiconductor lasers, or gas lasers (e.g. the argon laser, the helium neon laser, or the krypton laser), or a fiber laser.

The power at which the lasers used can usually operate is from 1 to 1200 watts, preferably from 10 to 500 watts, and particularly preferably from 12 to 100 watts. The focus of the laser beam is an important variable for the component resolution achievable by the process. Its radius is usually from 0.05 to 1 mm, preferably from 0.1 to 0.4 mm. However, a larger area of the focus or beam spot can also be advantageous in this process because, of course, the absorber intrinsically provides the selectivity. A larger area of focus or beam spot permits the irradiation of a layer to proceed more rapidly. Particular preference is given to the bars known from the diode laser, meaning that the energy is introduced by way of a relatively large rectangular area. To this end, the individual diode bars are combined to give what are known as stacks. The dimensions of the area across which the electromagnetic energy is introduced is then in the

millimeter, or indeed centimeter, range. By way of example, the dimensions of the rectangular area here may be from 0.1 to 100 mm in width; in length, they may advantageously be based on the height of the manufacturing chamber of the RP device, or else may be smaller, so that the construction area is scanned by the laser beam, as it were line-by-line. The irradiation velocity is usually from 10 to 10 000 mm/s, preferably from 700 to 5000 mm/s. This means the velocity of the laser focus beam across the powder bed; it may be possible to move the laser beam, e.g. by way of mirrors or by way of flexible conducting cables, or else to move the powder bed.

In order to be able to melt the inventive polymer powder layer-by-layer, the process parameters have to be selected appropriately. Examples of factors relevant here are the layer thickness, the power of the laser, and the irradiation velocity, and also the wavelength of the laser and the powder used, and in particular the absorber and the proportion of the absorber applied per unit area, inter alia.

It is advantageous to adapt the amount of absorber to the characteristics of the component; by way of example, less absorber may be applied in the middle of an area, particularly if by this stage there are some molten areas lying thereunder. Another advantage can be achieved if the first layer of a region to be melted is coated with absorber using a method different from that for the subsequent layers.

Absorption is defined as attenuation of the energy of a beam (light, electrons, etc.) on passage through matter. The dissipated energy here is converted into other forms of energy, e.g. heat. An absorber is correspondingly a piece of matter, or body, intended to absorb radiation (from [www.wissen.de](http://www.wissen.de)). An absorber in this text is intended to mean an additive which can absorb all of, or a major proportion of, laser radiation in the region from 100 to 3000 nm; it is sufficient here for portions of the absorber to exert this function.

The present invention therefore provides a process for producing a three-dimensional object, which comprises the steps of

- a) providing a layer of a pulverulent substrate
- b) controlling the temperature of the manufacturing chamber
- c) selective application of an absorber in a suspension or of a liquid absorber via an inkjet

process to the regions to be sintered

- d) application of other specific liquids or suspensions with certain properties
- e) selective melting of regions of the powder layer by means of introduction of electromagnetic energy via a laser of wavelength from 100 to 3000 nm preferably from 800 to 1070 nm, and more preferably with a YAG laser or a diode laser
- f) cooling of the molten and non-molten regions to a temperature which allows the moldings to be removed intact
- g) removal of the moldings,

and also provides moldings produced by this process. Steps a) to e) here are repeated until the desired molding has been fashioned layer-by-layer. Step b) is material-dependent and therefore optional. Step d) is likewise optional. The thickness of the layer applied is, by way of example, from 0.05 to 2 mm, preferably from 0.08 to 0.2 mm.

An alternative sequence consists in omitting step e) in the first layer and carrying it out from a second layer onward as an alternative after step a). This leads to fusion of the powder particles precisely in the boundary layer between the uppermost powder layer and the powder layer situated thereunder, giving particularly good bonding and moreover increasing the amount of processing latitude, because the result is substantial elimination of curl (roll-up of the edges or ends of the molten regions).

In another alternative sequence, step e) is not carried out in every cycle, but only at intervals, or in the extreme case indeed only once immediately before steps f) and g).

Surprisingly, it has been found to be relatively simple to produce three-dimensional objects from pulverulent substrates by means of a laser of wavelength from 100 to 3000 nm, by applying, to those regions to be bonded of a layer composed of a pulverulent substrate which does not absorb, or only poorly absorbs, the energy of the abovementioned laser, a material comprising an absorber which can absorb the laser energy and dissipate the absorbed energy in the form of heat to its surrounding substrate, thereby bonding, via fusion or sintering, the regions mentioned of the substrate of the layer, or, where appropriate, of a layer situated thereunder or thereabove. A printing head with one or more nozzles may be used to apply the

absorber and any other additives, for example using the piezoelectric effect or the bubble-jet principle, similar to that of an inkjet printer. The energy of the laser may be either focused or unfocused, giving the process a speed advantage.

5 The present invention also provides an apparatus for the layer-by-layer production of three-dimensional objects which comprises

- a movable apparatus for the layer-by-layer application of a pulverulent substrate to an operating platform or to a layer of a treated or untreated pulverulent substrate (2) which may at this stage be present on the operating platform,
- 10 - an apparatus (3) movable in the x, y plane, for the application of a material (4) comprising an absorber and optionally of other additives to selected regions of the layer composed of pulverulent substrate, and
- a laser of a wavelength from 100 to 3000 nm, preferably from 800 to 1070 m or from 1900 to 2100 nm, the introduction of energy being focused or unfocused, preferably unfocused.

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Alternatively, a movable operating platform may also be responsible for movements of the apparatuses or of the laser and of the operating platform relative to one another. It is also possible to use the operating platform to realize the relative movements in the x direction and to use the respective apparatus or the laser to realize the movements in the y direction, or vice

20 versa.

The inventive process has the advantage of being simpler, faster, more precise, and more advantageous than conventional processes. The controlled action of energy at certain sites on the layer is achieved via an absorber which is applied to the desired regions of the layer and

25 which is suitable for a laser of wavelength from 100 to 3000 nm.

The inventive process is a simple way of achieving automated layer-by-layer construction of a three-dimensional object via use of lasers of wavelength from 100 to 3000 nm in combination with a suitable absorber. Powder not treated with absorber can simply be reused. In addition,

30 specific properties, such as electrical conductivity, or inks can be included in the "printing" process. Using this method, the part can simultaneously be provided with selected properties.

The functional principle of the present inventive process for the production of three-dimensional objects is in principle based on the principle used in all of the other processes for rapid prototyping. The three-dimensional object is constructed in the form of layers. The method of construction is that parts of liquid layers (stereolithography) or powder layers (laser sintering) are secured or, respectively, melted, mutually or, respectively, with parts of layers situated thereunder, by introducing energy into these parts of the layers. The parts of the layers into which no energy has been introduced remain in the form of liquid or powder. Repetition of the application and melting process or, respectively, the process of securing powder or, respectively, liquid provides a three-dimensional object, layer-by-layer. Once the unconverted powder or, respectively, the unconverted liquid has been removed the result is a three-dimensional object whose resolution (in respect of contours) depends, if powder is used, inter alia on the layer thickness and the particle size of the pulverulent substrate used.

In contrast to the processes known hitherto, the energy is not supplied directly to the substrates to be bonded, but by way of an absorber, which absorbs the energy and dissipates it in the form of heat to its surrounding substrate. The result is a marked enlargement of the range of the pulverulent substrates that can be used, when comparison is made with conventional laser sintering. The inventive process introduces the energy in the form of laser radiation of wavelengths from 100 to 3000 nm, preferably from 800 to 1070 nm, or from 1900 to 2100 nm, and this is absorbed by the absorber, converted into heat, and dissipated to the pulverulent material which is directly adjacent to the substrate and which is incapable, or insufficiently capable, of absorbing the radiation from the abovementioned laser. "Insufficiently" means in the present instance that absorption of radiation via a laser of wavelength from 100 to 3000 nm cannot heat the pulverulent substrate sufficiently to enable it to bond via fusion or sintering to adjacent substrate particles, or that the time needed for this is very long. However, the heat dissipated from the absorber is sufficient to bond the pulverulent substrate adjacent to the absorber to itself and also to the absorber, via fusion or sintering. The inventive process thus produces three-dimensional objects via fusion or sintering of a pulverulent substrate.

The consequence of the application of the absorbers in step c), which is usually computer-controlled using CAD applications to calculate the cross-sectional areas, is that only treated pulverulent substrates are melted in a subsequent treatment step e). The material comprising

absorber is therefore applied only to selected regions of the layer from a), which are within the cross section of the three-dimensional object to be produced. The actual method of application may, for example, use a printing head equipped with one or more nozzles. After the final treatment step e) for the final layer, the inventive process gives a matrix, some of whose powder material has been bonded, and which releases the solid three-dimensional object after cooling and removal of the unbonded powder.

The inventive process is described by way of example below, but there is no intention that the invention be restricted thereto.

The inventive process for producing a three-dimensional object comprises the steps of

- a) providing a layer of a pulverulent substrate
- b) controlling the temperature of the manufacturing chamber
- c) selective application of an absorber in a suspension or of a liquid absorber via an inkjet process to the regions to be sintered
- d) application of other specific liquids or suspensions with certain properties
- e) selective melting of regions of the powder layer by means of introduction of electromagnetic energy via a laser of wavelength from 100 to 3000 nm preferably from 800 to 1070 nm or from 1900 to 2100 nm, and more preferably with a YAG laser or a diode laser
- f) cooling of the molten and non-molten regions to a temperature which allows the moldings to be removed intact
- g) removal of the moldings

Steps a) to e) here are repeated until the desired molding has been fashioned layer-by-layer. Step b) is material-dependent and therefore optional. Step d) is likewise optional. The thickness of the layer applied is, by way of example, from 0.05 to 2 mm, preferably from 0.08 to 0.2 mm.

An alternative sequence consists in omitting step e) in the first layer and carrying it out from the second layer onward as an alternative after step a). This leads to fusion of the powder particles precisely in the boundary layer between the uppermost powder layer and the powder layer situated thereunder, giving particularly good bonding and moreover increasing the amount



of processing latitude, because the result is substantial elimination of curl (roll-up of the edges or ends of the molten regions).

An example of a method for preparing the pulverulent layer is application of a powder material  
5 as substrate to a base plate or to an existing layer treated in steps b) to e), if such a layer is present. The method of application may be doctoring, rolling, or broadcasting and subsequent stripping, or a similar method. The single precondition with which the provision of the layer has to comply is that the layer has uniform height. The height of the layer provided in step a) is preferably smaller than 3 mm, with preference from 20 to 2000  $\mu\text{m}$ , and particularly preferably  
10 from 80 to 200  $\mu\text{m}$ . The height of the layers here determines the resolution and therefore the smoothness of the external structure of the three-dimensional object produced. The base plate, or else the apparatus for providing the layer, may be designed with adjustable height so that after the step d) or e) has been carried out, either the resultant layer can be lowered by the height of the layer to be applied next or the apparatus can be raised by the difference in height  
15 of the next layer over the preceding layer.

Powder material preferably used as pulverulent substrate has a median grain size ( $d_{50}$ ) of from 10 to 150  $\mu\text{m}$ , particularly preferably from 20 to 100  $\mu\text{m}$ , and very particularly preferably from 40 to 70  $\mu\text{m}$ . However, depending on the intended use, it can be advantageous to use a powder  
20 material comprising particularly small particles, and also comprising particularly large particles. In order to realize three-dimensional particles with maximum resolution and maximum surface smoothness, it can be advantageous to use particles whose median particle size is from 10 to 45  $\mu\text{m}$ , preferably from 10 to 35  $\mu\text{m}$ , and very particularly preferably from 20 to 30  $\mu\text{m}$ .

25 It is very difficult to process fine material smaller than 20  $\mu\text{m}$ , in particular smaller than 10  $\mu\text{m}$ , because it does not flow, and the bulk density falls drastically, and this can cause more production of cavities. To ease operation, it can be advantageous to use particles whose median size is from 60 to 150  $\mu\text{m}$ , preferably from 70 to 120  $\mu\text{m}$ , and very particularly preferably from  
30 75 to 100  $\mu\text{m}$ .

The pulverulent substrate used preferably comprises powder material which was prepared by

milling, precipitation, and/or anionic polymerization, or by a combination of these. This may be followed by a fractionation and/or addition of a powder-flow aid. A mechanical post-treatment can likewise be advisable, for example in a high-speed mixer, in order to round the sharp-edged particles produced during the milling process, thus making it easier to apply thin layers.

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The particle size distribution may be selected as desired for the stated median grain sizes of the powder materials. It is preferable to use powder materials which have a broad or narrow grain size distribution, preferably a narrow grain size distribution; bimodal grain size distributions are also advantageous. Particularly preferred pulverulent materials for use in the inventive process have a grain size distribution in which the polydispersity, defined as the difference between the  $D_{90}$  value and the  $D_{10}$  value, based on the  $D_{50}$  value, is from 0.05 to 15, preferably from 0.1 to 10, and particularly preferably 0.5 to 5. An example of the method for determining the grain size distribution is laser diffraction, using the Malvern Mastersizer S. The grain size distribution can be adjusted via conventional classification processes, e.g. pneumatic separation. Maximum narrowness of grain size distribution in the inventive process gives three-dimensional objects which have a very uniform surface and have very uniform pores, if pores are present.

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At least some of the pulverulent substrate used can be amorphous, crystalline, or semicrystalline. Aromatic structures may moreover be present. Preferred powder material has a linear or branched structure. Particularly preferred powder material used in the inventive process comprises at least some material whose melting point is from 50 to 350°C, preferably from 70 to 200°C.

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Suitable substrates in the inventive process are substances which, when compared with the selected absorber, are less effectively heated by radiation via a laser of wavelength from 100 to 3000 nm. The pulverulent substrate used should moreover have adequate flowability in the molten state. Pulverulent substances which may in particular be used are polymers or copolymers selected from polyester, polyvinyl chloride, polyacetal, polypropylene, polyethylene, polystyrene, polycarbonate, polybutylene terephthalate, polyethylene terephthalate, polysulfone, polyarylene ether, polyurethane, polylactides, thermoplastic elastomers, polyoxyalkylenes, poly(N-methylmethacrylimides) (PMMI), polymethyl

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methacrylate (PMMA), ionomer, polyamide, copolyester, copolyamides, silicone polymers, terpolymers, acrylonitrile-butadiene-styrene copolymers (ABS), and mixtures thereof.

The pulverulent substrate used in the inventive process particularly preferably comprises a material which comprises a polyamide, preferably at least one nylon-6, nylon-11, and/or nylon-12, or which comprises a copolyester or comprises a copolyamide. Particularly dimensionally stable three-dimensional moldings can be produced by using polyamides. Particular preference is given to the use of nylon-12 powder, preferably prepared as described in DE 197 08 946, or else DE 44 21 454, and particularly preferably having a melting point and an enthalpy of fusion as stated in EP 0 911 142. They may be regulated, semiregulated, or unregulated, preferably unregulated. They may have a linear aliphatic structure or else have aromatic units. Preferred copolyamides or copolyesters used are those obtainable from Degussa AG with the trademark VESTAMELT. Particularly preferred polyamides have a melting point, determined by means of differential scanning calorimetry (DSC) of from 76 to 159°C, preferably from 98 to 139°C, and very particularly preferably from 110 to 123°C. By way of example, the copolyamides may be prepared via polymerization of mixtures of suitable monomers, e.g. selected from laurilactam and/or caprolactam, as bifunctional component, suberic acid, azelaic acid, dodecanedioic acid, adipic acid, and/or sebacic acid as component bearing an acid function, and 1,6-hexanediamine, isophoronediamine and/or methylpentamethylenediamine as diamine. Aromatic units may also be used. Suitable other comonomers and rules for their selection are known to the person skilled in the art and described, by way of example, in J. G. Dolden, *Polymer* (1976, 17), pp. 875-892.

In order to improve the processibility of the pulverulent substrates, it can be advantageous to use a powder material which comprises additives. These additives may be powder-flow aids, for example. The pulverulent substrate used particularly preferably comprises from 0.05 to 5% by weight, with preference from 0.1 to 1% by weight, of additives. Examples of powder-flow aids may be fumed silicas, stearates, or other powder-flow aids known from the literature, e.g. tricalcium phosphate, calcium silicates,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{MgCO}_3$ , or  $\text{ZnO}$ . By way of example, fumed silica is supplied by Degussa AG with the trade name Aerosil®. It can also be advantageous, if absorber is indeed present in the pulverulent substrate used, but the amount of absorber is less than that which leads to undesired melting of unselected regions. The person

skilled in the art can easily establish limits via exploratory experiments.

Alongside, or instead of, these in part inorganic powder-flow aids or other additives, inorganic fillers may also be present in a pulverulent substrate used according to the invention. The use of  
5 these fillers has the advantage that they substantially retain their shape through the treatment during the bonding process and therefore reduce the shrinkage of the three-dimensional object. Another possibility provided by the use of fillers is modification of the plastic and physical properties of the objects. For example, use of powder material which comprises metal powder can adjust not only the transparency and color of the object but also its magnetic or electrical  
10 properties. Examples of fillers which may be present in the powder material are glass particles, ceramic particles, or metal particles. Examples of typical fillers are metal granules, aluminum powder, steel shot or glass beads. It is particularly preferable to use powder materials in which glass beads are present as filler. In one preferred embodiment, the inventive powder material comprises from 1 to 70% by weight, preferably from 5 to 50% by weight, and very particularly  
15 preferably from 10 to 40% by weight, of fillers.

Alongside, or instead of, inorganic powder-flow aids or fillers, inorganic or organic pigments may also be present in a pulverulent substrate used according to the invention. These pigments may be not only color pigments which determine the perceived color of the three-dimensional  
20 object to be produced, but also pigments which affect the other physical properties of the three-dimensional articles to be produced, e.g. magnetic pigments or conductivity pigments, for example conductivity-modified titanium dioxide or tin oxide, which alter the magnetic properties and, respectively, the conductivity of the article. However, the powder material to be used particularly preferably comprises inorganic or organic color pigments selected from chalk,  
25 ocher, umber, green earth, burnt sienna, graphite, titanium white (titanium dioxide), white lead, zinc white, lithopone, antimony white, carbon black, iron oxide black, manganese black, cobalt black, antimony black, lead chromate, mennium, zinc yellow, zinc green, cadmium red, cobalt blue, Prussian blue, ultramarine, manganese violet, cadmium yellow, Schweinfurter green, molybdate orange, molybdate red, chrome orange, chrome red, iron oxide red, chromium oxide  
30 green, strontium yellow, metallic-effect pigments, pearlescent pigments, luminescent pigments using fluorescent and/or phosphorescent pigments, umber, gamboge, animal charcoal, Cassel brown, indigo, chlorophyll, azo dyes, indigoids, dioxazine pigments, quinacridone pigments,

phthalocyanine pigments, isoindolinone pigments, perylene pigments, perinone pigments, metal complex pigments, alkali blue pigments, and diketopyrrolopyrrole. By way of example, further information relating to pigments which may be used may be found in Römpp Lexikon Chemie [Römpp Chemical Encyclopedia] - Version 2.0, Stuttgart/New York: Georg Thieme Verlag  
5 1999, and in the references given therein. However, the concentration of these pigments in the powder must be selected so as to give, at most, very little absorption of the energy introduced; it must be below the threshold at which the powder particles sinter via the heat transferred to them.

- 10 Other substances which may be used as powder material are those which may be regarded as a specialized form of the abovementioned fillers or pigments. In powder material of this type, the powder comprises grains composed of a first material with a size smaller than the abovementioned dimensions for the powder material. The grains have been coated with a layer of a second material, the thickness of the layer having been selected in such a way that the  
15 powder material composed of the combination of grain of the first material and coating of the second material has the size stated above. The grain of the first material preferably have a size which deviates from the size of the powder material by less than 25%, preferably less than 10%, and particularly preferably less than 5%. The second material, which is the coating of the grains, is a material which, when compared with the selected absorber, is less effectively heated  
20 by radiation via the laser of wavelength from 100 to 3000 nm. The second material should moreover have adequate flowability in the heated state and be capable of sintering or fusion via exposure to heat, this heat being provided by the absorber. The coating material present in the pulverulent substrates (the powder materials) may in particular be the abovementioned polymers or copolymers, preferably selected from polyester, polyvinyl chloride, polyacetal,  
25 polypropylene, polyethylene, polystyrene, polycarbonate, polybutylene terephthalate, polyethylene terephthalate, polysulfone, polyarylene ether, polyurethane, thermoplastic elastomers, polylactides, polyoxyalkylenes, poly(N-methylmethacrylimides) (PMMI), polymethyl methacrylate (PMMA), ionomer, polyamide, copolyester, copolyamides, silicone polymers, terpolymers, acrylonitrile-butadiene-styrene copolymers (ABS), and mixtures  
30 thereof. The first material of this specialized form of the powder material may encompass grains, by way of example, composed of sand, ceramic, metal, and/or alloys. A particularly preferred powder material of this type is phenolic-resin-coated sand or thermoplastic-coated

sand, known as molding sand.

If the absorber is capable of transferring a sufficient amount of heat, it is likewise possible for the powder material used to comprise metal powder, in particular powder of low-melting-point metals, e.g. lead or tin, or alloys which comprise, by way of example, tin or lead. This powder material, too, preferably has the abovementioned dimensions. If metal powder is used, it is first necessary to check whether the metal is suitable for treatment with a laser of wavelength from 100 to 3000 nm, or whether sparking or other undesirable effects occur. This check can be carried out via simple preliminary experiments.

The inventive process can therefore produce three-dimensional objects which can be equipped with one or more functionalized layers. An example of a functionalization is the provision of conductive properties to the entire molding or else only to certain regions via application of appropriate pigments or substances, by analogy with the absorber, or via provision of a layer composed of a pulverulent substance in which these pigments are present.

The method for applying the absorber can be based on that described in WO 01/38061 for application of the inhibitor. The absorber is preferably applied using an apparatus movable in the x,y plane. The apparatus has the capability to deposit liquid and/or pulverulent absorbers at defined sites on the layer provided in step a). By way of example, the apparatus may be a printing head, as used in an inkjet printer and having one or more nozzles. The guiding of the apparatus for the positioning of the printing head may likewise take place in the same way as the guiding of the printing head in an inkjet printer. Using this apparatus, the absorber is applied at those sites on the layer provided in step a) at which the substrate is to be bonded via sintering or fusion.

Absorbers which can be used in the inventive process are any of those which are heated via electromagnetic radiation from a laser of wavelength from 100 to 3000 nm.

In the simplest case, the absorber comprises what is known as a colorant. A colorant is any of the coloring substances to DIN 55944, these being divisible into inorganic and organic colorants, and also into natural and synthetic colorants (see Römpps Chemielexikon [Römpps's

Chemical Encyclopedia], 1981, 8th edition, p. 1237). According to DIN 55943 (Sept. 1984) and DIN 55945 (Aug. 1983), a pigment is an inorganic or organic colorant whose color is non-neutral or neutral and which is practically insoluble in the medium in which it is used. Dyes are inorganic or organic colorants whose color is non-neutral or neutral and which are soluble in  
5 solvents and/or in binders.

However, the absorber may also gain its absorbent action by comprising additives. By way of example, these may be flame retardants based on melamine cyanurate (Melapur from DSM) or based on phosphorus, preference being given to phosphates, phosphites, phosphonites, or elemental red phosphorus. Other suitable additives are carbon fibers, preferably ground, glass  
10 beads, including hollow beads, or kaolin, chalk, wollastonite, or graphite.

The absorber present in the inventive powder preferably comprises carbon black or CHP (copper hydroxide phosphate), or chalk, animal charcoal, carbon fibers, graphite, flame retardants, or interference pigments as principal component. Interference pigments are what are  
15 known as pearl-luster pigments. Using the natural mineral mica as a basis, they are encapsulated with a thin layer composed of metal oxides, such as titanium dioxide and/or iron oxide, and are available with a median grain size distribution of from 1 to 60  $\mu\text{m}$ . By way of example, interference pigments are supplied by Merck with the name Iriodin. The Iriodin product line from Merck encompasses pearl-luster pigments and metal-oxide-coated mica  
20 pigments, and also the subclasses of: interference pigments, metallic-luster special-effect pigments (iron oxide coating on the mica core), silvery white special-effect pigments, gold-luster special-effect pigments (mica core coated with titanium dioxide and with iron oxide). The use of Iriodin grades in the Iriodin LS series is particularly preferred, namely Iriodin LS 820, Iriodin LS 825, Iriodin LS 830, Iriodin LS 835, and Iriodin LS 850. The use of Iriodin LS  
25 820 and Iriodin LS 825 is very particularly preferred.

Other suitable materials are: mica or mica pigments, titanium dioxide, kaolin, organic and inorganic color pigments, antimony(III) oxide, metal pigments, pigments based on bismuth oxychloride (e.g. the Biflair series from Merck, high-luster pigment), indium tin oxide (nano-  
30 ITO powder from Nanogate Technologies GmbH or AdNano<sup>™</sup> ITO from Degussa), AdNano<sup>™</sup> zinc oxide (Degussa), lanthanum hexachloride, ClearWeld® (WO 0238677), and also commercially available flame retardants which comprise melamine cyanurate or comprise

phosphorus, preferably comprising phosphates, phosphites, phosphonites, or elemental (red) phosphorus.

If the intention is to avoid any adverse effect on the intrinsic color of the powder, the absorber  
5 preferably comprises interference pigments, particularly preferably from the Iriodin LS series from Merck, or Clearweld®.

The chemical term for CHP is copper hydroxide phosphate; this is used in the form of a pale green, fine crystalline powder whose median grain diameter is just 3  $\mu\text{m}$ .

10 The carbon black may be prepared by the furnace black process, the gas black process, or the flame black process, preferably by the furnace black process. The primary particle size is from 10 to 100 nm, preferably from 20 to 60 nm, and the grain size distribution may be narrow or broad. The BET surface area to DIN 53601 is from 10 to 600  $\text{m}^2/\text{g}$ , preferably from 70 to  
15 400  $\text{m}^2/\text{g}$ . The carbon black particles may have been subjected to oxidative post-treatment to obtain surface functionalities. They may be hydrophobic (for example Printex 55 or flame black 101 from Degussa) or hydrophilic (for example FW20 carbon black pigment or Printex 150 T from Degussa). They may have a high or low level of structuring; this describes the degree of aggregation of the primary particles. Specific conductive carbon blacks can be used  
20 to adjust the electrical conductivity of the components produced from the inventive powder. Better dispersibility in both the wet and the dry mixing processes can be utilized using carbon black in bead form. It can also be advantageous to use carbon black dispersions.

Animal charcoal is an inorganic black pigment comprising elemental carbon. It is composed of  
25 from 70 to 90% of calcium phosphate and from 30 to 10% of carbon. Density is typically from 2.3 to 2.8  $\text{g/ml}$ .

The absorbers may, by way of example, be in pellet form or in powder form or liquid form. For distribution within a printing head with one or more fine nozzles it is advantageous for the  
30 particles to have maximum fineness, and therefore excessively coarse particles or pellets can be milled or further milled, preferably at low temperatures, and then optionally classified.



These additives used here as absorbers are obtainable, by way of example, from Merck with the name Iriodin®. Carbon black means commercially available standard carbon blacks, such as those supplied by the companies Degussa AG, Cabot Corp., or Continental Carbon.

- 5    Commercially available examples of suitable absorbers in a general sense are Iriodin® LS 820 or Iriodin® LS 825, or Iriodin® LS 850 from Merck. Examples which may be mentioned for the carbon black are Printex 60, Printex A, Printex XE2, or Printex Alpha from Degussa. Degussa likewise supplies suitable CHP with the trade name Vestodur FP-LAS.
- 10   It is advantageous to prepare a liquid which comprises the absorber and which can be applied in a printing head, like an ink, to the pulverulent substrate. It is possible to use mixtures of solid, liquid, or solid and liquid absorbers. It can also be advantageous for absorbers in solid form to be suspended in liquids which are not absorbers, in order to achieve better distribution of the absorber in solid form over the entire depth of the layer provided. It is also advantageous
- 15   to add specific rheological additives which inhibit sedimentation of the solid absorber in the liquid. Another advantage can be achieved if surfactants, such as alkylphenol ethoxylates, fatty alcohol ethoxylates, fatty acid ethoxylates, fatty amine ethoxylates, are added to the absorber, in particular to the liquid absorber or to the suspension of a solid absorber in a liquid, in order to improve the wetting of the substrate. The liquid may - with no intention of restricting the
- 20   invention thereto - comprise water, preferably distilled, or alcohols, such as isopropanol, glycerol, diethylene glycol.

The use of commercially available dispersions can be particularly advantageous, examples being those from the Derussol product line from Degussa.

The use of a liquid absorber, such as Clearweld®, is likewise advantageous.

25

- Many absorber/substrate combinations may moreover be considered for use in this inventive process, but an important factor for the process is an adequately large difference between absorber and substrate in the ability to be excited via radiation from the laser of wavelengths from 100 to 3000 nm, so that the matrix obtained at the end of the process has a clear boundary
- 30   between molten (i.e. absorber-treated) substrate and non-molten substrate. This is the only way of ensuring that the three-dimensional object produced has a sufficiently smooth outline and can be released easily from the unbonded substrate. The precision of the process is superior to

the laser sintering process, by way of example, because it permits much greater control of introduction of the energy.

In order to allow a sufficient amount of heat transfer from absorber to the substrate for a sufficient time, the boiling point of the absorber, or in the case of a mixture of absorbers the boiling point of at least one absorber, should be higher than the melting point of the substrate used. The parameters relating to the application of the absorber-containing liquid, and the properties of the powder and of the absorber, and also of the entire liquid, have to be balanced with respect to one another in order that the absorber does not permeate through the layers but is absorbed exclusively by the powder regions to be wetted. An example of a balancing method is adjustment of the viscosity, and the amount used, of the absorber-containing liquid. The amount of the liquid used here is in particular dependent on the thickness of the powder layer, on the porosity of the powder, and on the particle size and the content of liquid or solid absorber. The ideal amount and viscosity for each of the combinations of materials can be determined in simple preliminary experiments. To adjust the viscosity, use can be made of known thickeners, such as fumed silicas, or else organic agents. It is also advantageous for the absorber-containing liquid to comprise wetting agents and/or biocides and/or moisture retainers. The liquid may comprise, by way of example, water, preferably distilled, or solvents or alcohols. The liquid comprising absorber(s) may remain in the melt and, respectively, in the molding. This can indeed be advantageous when reinforcement occurs or when other properties are adjusted via the absorber (electrical or magnetic conductivity). The carrier liquid, if such a liquid has been used, either likewise remains within the component or vaporizes or evaporates. The absorbers, liquids, and other additives used are advantageously non-toxic substances which permit problem-free operation in an office environment.

The energy needed for heating the absorber is introduced in the form of electromagnetic radiation in the range from 100 to 3000 nm, preferably from 800 to 1070 nm, or from 1900 to 2100 nm. It can be advantageous for the layers to be sintered to be brought to an elevated temperature, via introduction of heat, or to be kept at an elevated temperature below the melting or sintering point of the polymer used. This method can reduce the amount of electromagnetic energy for the selective melting process. A precondition for this is the presence of a temperature-controlled construction space, but it reduces the likelihood of curl (roll-up of the corners and edges out of the plane of construction, which can make it impossible to repeat

step a)). It can also be advantageous for the absorber or the absorber-containing liquid to be preheated.

The radiation required for the inventive process is generated via a laser which emits  
5 electromagnetic radiation in the range from 100 to 3000 nm. These lasers may be as described above, their beam mostly being focused, for example using mirrors, lenses, and/or optical conductors. However, they may also be lasers which do not necessarily emit a focused laser beam, e.g. diode lasers, which can also irradiate relatively large, mostly rectangular areas with adequate power via stacking of diode bars.

10 An unfocused or indeed spread introduction of energy is very advantageous in the present process, however, because, of course, the selectivity is intrinsically provided for each layer by way of the absorber or, respectively, absorber-containing liquid applied selectively via an inkjet process. This makes the process faster.

15 The inventive process can produce three-dimensional moldings. After conclusion of the inventive process, these pre-dimensional objects produced layer-by-layer are finally present within a matrix which is formed from a plurality of layers. The object can be removed from this matrix, which is composed of bonded and unbonded pulverulent substrate and also of absorber, while the unbonded substrate can be reintroduced, where appropriate after treatment, e.g. via  
20 sieving. The inventive moldings may comprise fillers, selected from glass beads, silicas, or metal particles.

The inventive process is preferably carried out in an inventive apparatus for the layer-by-layer production of three-dimensional objects, which comprises

- 25
- a movable apparatus for the layer-by-layer application of a pulverulent substrate to an operating platform or to a layer of a treated or untreated pulverulent substrate (2) which may at this stage be present on the operating platform,
  - an apparatus (3) movable in the x, y plane, for the application of a material (4) comprising an absorber and optionally of other additives to selected regions of the
  - 30 layer composed of pulverulent substrate, and
  - a laser of a wavelength from 100 to 3000 nm, preferably from 800 to 1070 nm, or from 1900 to 2100 nm, the energy here being introduced in focused or unfocused

form, preferably unfocused.

As an alternative, a movable operating platform may also be responsible for movements of the apparatus and, respectively, of the laser and of the operating platform relative to one another. It is also possible to use the operating platform to realize the relative measurements in the x direction and to use the respective apparatus or, respectively, the laser to realize the movements in the y direction, or vice versa.

The apparatus has preferably been equipped with a plurality of storage vessels from which the pulverulent substrate to be processed can be introduced into the apparatus for generating the layers and the absorber(s) used can be introduced into the apparatus for the application of an absorber to selected regions of the layer composed of pulverulent substrate. By using printing heads with one or more nozzles and providing a mixer, it is possible for the absorber mixture used at particular zones of the layer, e.g. at particularly filigree regions or, for example, at the edge of the object to be produced, to differ from that used in the core region of the object to be produced. Using this method, there can be different introduction of energy at different positions in the layer.

The present invention also provides the powder material as described above, suitable for use in the inventive process and in particular featuring a median grain size from 10 to 150  $\mu\text{m}$  and comprising at least one polymer or copolymer selected from polyester, polyvinyl chloride, polyacetal, polypropylene, polyethylene, polystyrene, polycarbonate, polybutylene terephthalate, polyethylene terephthalate, polysulfone, polyarylene ether, polyurethane, thermoplastic elastomers, polylactides, polyoxyalkylenes, poly(N-methylmethacrylimides) (PMMI), polymethyl methacrylate (PMMA), ionomer, polyamide, copolyester, copolyamides, silicone polymers, terpolymers, acrylonitrile-butadiene-styrene copolymers (ABS), and mixtures thereof.

Figure 1 gives a more detailed explanation of the inventive process and the inventive apparatus, but there is no intention that the invention be restricted to this embodiment. Fig. 1 is a diagram of the inventive apparatus. Untreated pulverulent substrate (2), forming an initial charge in a storage vessel (1), is built up to give a matrix (8) on a movable base (6). By means of a doctor

blade (2), the substrate is distributed to give thin layers on the movable base or, respectively, on previously applied layers. The absorber (4) or, respectively, the absorber-containing liquid is applied to selected regions of the layer composed of pulverulent substrate by way of an apparatus (3) movable in the x, y plane. After each treatment with an absorber, a fresh layer of the pulverulent substrate is applied. Those sites on the applied substrate that have been treated with the absorber are bonded by means of energy introduced at a wavelength of from 100 to 3000 nm via a laser or another energy source (5), to give a three-dimensional object, e.g. a cup (7). This step can also take place before the application of the next powder layer.

- 10 The examples below provide more detailed explanation of the inventive process, but there is no intention that the invention be restricted thereto.

**Example 1: Production of a plaque from a copolyamide by means of a diode laser**

- A model for a plaque of dimensions 3\*20\*1 mm<sup>3</sup> is produced from a copolyamide powder (VESTAMELT 170, Degussa AG, Marl) in the apparatus described via Fig. 1. The absorber used comprises a suspension based on CHP (Vestodur FP-LAS from Degussa), comprising 40% by weight of distilled water, 40% by weight of CHP, and 20% by weight of isopropanol. The apparatus has an operating temperature of about 40°C. The wavelength of the diode laser is 940 nm, the dimensions of the beam spots being 1.5 × 3.5 mm. The thickness of the layer is 0.15 mm. For each layer, the diode laser is moved line-by-line across the manufacturing platform at a velocity of 700 mm/sec, using a power level of 200 watts. The D<sub>50</sub> value for the powder is 60 µm.

25 **Example 2: Production of a plaque from nylon-12 by means of a diode laser**

- Another plaque of dimensions 3\*20\*1 mm<sup>3</sup> is produced from a nylon-12 powder (EOSINT P PA 2200, EOS GmbH Electro Optical Systems, Krailling, Germany) in the apparatus described above. The absorber used comprises Iriodin® LS 825. The liquid distributed by the inkjet process was composed of 30 percent by weight of Iriodin, 59% of isopropanol, and 1% of Pril (Henkel). The apparatus has an operating temperature of about 160°C. The wavelength of the spread diode laser is 940 nm, and the dimensions of the beam spot are 1.5 × 3.5 mm. The application depth of the powder layers was 0.15 mm. For each layer, the diode laser traverses

the manufacturing plane line-by-line at a velocity of 500 mm/sec, using a power level of 200 watts. The powder used had a  $d_{50}$  value of 55  $\mu\text{m}$ .

**Example 3: Production of a plaque composed of nylon-12 by means of an Nd:YAG laser**

5 An open-topped box,  $10 \times 10$  cm, was provided with a base which can be moved by way of a spindle. The base was moved to a position half a centimeter from the upper edge; the remaining space was filled with powder, which was smoothed using a metal plate. The apparatus was placed in the manufacturing chamber of an Nd:YAG laser Star Mark 65 (producer: Carl Basel Lasertechnik). The opening of the box was half covered, and the absorber-containing liquid  
10 was applied using an atomizer (commercially available, for perfume). Care needs to be taken here that wetting is uniform and that no dripping occurs. The cover was then removed and the entire area was scanned with the laser energy.

The next steps, turning of the spindle to lower the base by 0.1 mm, and application of the next powder layer, smoothing, covering and applying the absorber to half of the material, removing  
15 the cover and then again irradiating via the Nd:YAG laser to melt the powder, were repeated a number of times.

The polymer used was a nylon-12 from Degussa, namely Vestosint 2157. The absorber used comprised Printex 60, likewise from Degussa. 10 parts of Printex 60 were mixed here with 70 parts of distilled water, 18 parts of isopropanol, and 2 parts of Pril (Henkel). The apparatus  
20 has an operating temperature of about 165°C. The wavelength of the Nd:YAG laser is 1064 nm. For each layer, the Nd:YAG traverses the manufacturing plane selectively at a velocity of 300 m/sec, using a power level of 30 watts. The powder used had a  $d_{50}$  value of 55  $\mu\text{m}$ . This experiment produced a plaque from the region provided with absorber. The powder not treated with absorber did not melt. However, there remained a need to optimize, in  
25 particular, the temperature profile, because curl occurred by virtue of the lack of automated handling and the application of cold absorber.